

Docket No. KPC-289
Serial No. 09/804,293

PATENT APPLICATION


specification filed with the original application papers. The reason for the changes is set forth in the Petition under 37 CFR §1.182, which is filed concurrently herewith. The substitute specification with Abstract is attached hereto as Appendix I. A marked-up version of the specification is enclosed which shows each of the changes incorporated into the substitute specification as Appendix II. Accordingly, entry of the substitute specification is respectfully requested.

The original claims 1-9 have been cancelled and new claims 10-20 have been added for the Examiner's consideration. Claims 10 to 20 are now pending in this application. A marked-up version of claims are attached hereto as Appendix III.

Prompt and favorable examination of this application, as amended by this preliminary amendment, is respectfully requested.

If the Examiner has any comments or suggestions that could place this application into even better form, the Examiner is encouraged to contact the Applicant's undersigned representative at the number listed below.

Respectfully submitted,



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APPENDIX II

MARKED-UP VERSION OF SPECIFICATION

[SETTING COMPOSITION, AND INK, PAINT AND ADHESIVE CONTAINING
THE SAME COMPOSITION] COLD SETTING COMPOSITION

DO NOT
ENTER

11/12/02

[Field of the Invention]

5 The present invention relates to a curable resin composition to be used for resin processing and molding which has decomposability and does not prevent recycling of itself or materials to which it is attached, and a resin to be used for paints, inks, adhesives and the like containing the resin composition.

10

Background of the Invention

Currently, a large quantity of resins is used for preparing paints, inks, adhesives and resin processed moldings. These are generally used once and then thrown away, and their treatment after use such as their decomposition is not considered. Therefore, it is hindered to recycle not only the resins themselves but also the materials that are covered with these resins or to which these resins are attached.

15

20 For improving the above point, the present inventor found that the chemical structure represented by formula (1) below in a molecule could easily decompose by the contact with an acid, water and a solvent at the same time. Thereafter, a method for removing it was applied for a patent, i.e., Japanese Patent Application No. 10-219156/1998.

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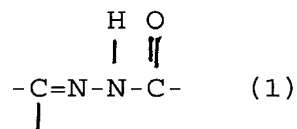
Summary of the Invention

The present invention relates to a resin composition to which such method for such removal is applicable. At present, as a system to which the method for removal is]

[applicable, there is paint where a resin containing a carbonyl group is cured with a dihydrazide compound, for example. However, since the chemical structure of formula (1) is formed at the curing in that method, the paint cannot
5 be applied to the case where crosslinking is not required or where crosslinking is carried out by other means such as light, heat or the like, so that its usable range is limited.

As a result of extensive studies for improving the defect, the present inventor has found that the problem is
10 solved by incorporating the linkage in a resin itself, and therefore has accomplished the invention.

The present invention relates to a curable composition containing a resin (A) having the structure of the structural formula represented by the formula (1) below:



and a crosslinkable functional group or groups in one molecule. Particularly, the structure of the structural formula represented by formula (1) present in the resin (A) may be formed by the reaction of a carbonyl group with a
25 hydrazide group or a semicarbazide group.

Further, the crosslinkable functional group (or groups) present in the resin (A) may be one type or two or more types selected from a polymerizable double bond, hydroxyl group, carboxyl group, isocyanate group, amino group,
30 thiol group, epoxy group, triazine group, dimide group, silanol group, an alkoxysilyl group, methylol group, an]

[alkylmethylol group, an acetoalkoxy group, carbonyl group, hydrazide group, a blocked isocyanate group, a blocked carboxyl group and a blocked hydroxyl group.

Still further, the resin (A) may be that having one
5 or more structures of the structural formula represented by the formula (1) between the crosslinkable functional groups.

The resin may be a resin having the structure of the structural formula represented by formula (1) in the backbone of the resin and the crosslinkable functional group in the
10 side chain.

Additionally, the resin (A) may be a resin having the same number of the structure or structures of the structural formula represented by formula (1) and the crosslinkable functional group or groups.

15 Preferred Embodiments of the Invention

An organic resin which contains the structure of the structural formula represented by formula (1) and a coexisting crosslinkable functional group may be used as the resin (A). The examples of the organic resin may include
20 such as an acryl resin, alkyd resin, vinyl resin, urethane resin, epoxy resin, polyester resin or polyether resin.

The structural formula represented by formula (1) can be decomposed in the presence of moisture, under an acidic atmosphere, or preferably in an organic solvent, and
25 can be formed, for example, by a reaction of a compound containing carbonyl group with a compound containing hydrazide group and/or a compound containing semicarbazide group. Furthermore, the crosslinkable functional group may be introduced, for example, by using a compound containing]

[carbonyl group or hydrazide group which also possesses the crosslinkable functional group.

Examples of the compound containing carbonyl group include such as diacetone alcohol or 4-hydroxy-2-butanone.

5 Examples of the compound containing hydrazide group include such as iminodiacetic acid dihydrazide, adipic acid dihydrazide, carbohydrazide, glutaric acid dihydrazide, azelaic acid dihydrazide, dodecanoyldihydrazide, cyclohexanetricarboxylic acid trihydrazide, tartaric acid
10 dihydrazide or crotonic acid dihydrazide. Diacetone acryl amide, acrolein and the like may be mentioned as the compound containing carbonyl group which further possesses a polymerizable double bond as the crosslinkable functional group.

15 More concretely, in the case of polymerization-type resins such as an acryl resin and vinyl resin, the resin (A) can be obtained by copolymerizing polymerizable unsaturated monomers each having the structure of the structural formula represented by formula (1) and a crosslinkable functional
20 group, or by addition or condensation reaction of compounds each having the structure of the structural formula represented by formula (1) and a crosslinkable functional group to a polymerization-type resin. In the case of condensation-type resins such as alkyd resins and polyester
25 resins, the resin (A) can be obtained by using a reaction product of a compound containing carbonyl group and hydroxyl group or carboxyl group with a compound containing two or more hydrazide groups and/or semicarbazide groups as at least part of polyhydric alcohol or polybasic acid. In the case of]

[urethane resins, the resin (A) can be obtained by using a reaction product of a compound containing carbonyl group and hydroxyl group with a compound containing hydrazide group and/or semicarbazide group as a polyhydric alcohol and
5 reacting it with a polyisocyanate. In the case of epoxy resins, the resin (A) can be obtained by adding a reaction product of a compound containing carbonyl group with a compound containing hydrazide group and/or semicarbazide group to an epoxy resin or by adding a compound having amino
10 group or carboxyl group and hydrazide group to an epoxy group and subjecting to dehydrative condensation of a compound having carbonyl group with the hydrazide group. In the case of polyether resins, the resin (A) can be obtained in a similar manner to the above epoxy resin case using a
15 polyether resin having epoxy groups.

The crosslinkable functional group to be introduced into the resin (A) at the same time when the structure of the structural formula represented by formula (1) is introduced is not particularly limited, and may be exemplified by a
20 polymerizable double bond, hydroxyl group, carboxyl group, isocyanate group, amino group, thiol group, epoxy group, triazine group, dimide group, silanol group, alkoxysilyl group, methylol group, alkylmethylol group, acetoalkoxy group, carbonyl group, hydrazide group, locked isocyanate group,
25 blocked carboxyl group and blocked hydroxyl group. One type or two or more types of these groups may be introduced in the same molecule.

The resin (A) containing a polymerizable double bond can be by itself cured with crosslinking by oxidative]

[polymerization or irradiation with an active energy beam such as light or electron beam. The other crosslinkable functional group is preferably used in combination with a crosslinking agent (B) having a functional group reactive thereto.

The examples of the crosslinking agent (B) include polyisocyanate compounds, polyepoxy compounds, melamine resins, urea resins, benzoguanamide resins, polyoxy compounds, polycarbonyl compounds, polyhydrazine compounds, polyamine compounds, polysemicarbazide compounds, polydimide compounds, polyacetoacetoxo compounds, polysilanol compounds, polyalkoxysilyl compounds and the like. Two or more of them may be used in combination.

The curable resin composition of the present invention may contain a coloring pigment, an extender, a thickening agent, a defoaming agent, an organic solvent, water, a plasticizer, a resin other than the above, if necessary.

The method for curing the curable resin composition of the present invention may be optionally selected depending on the crosslinkable functional group of the resin (A) and the composition of the crosslinking agent (B), and the resin composition can be cured under room temperature, heating, irradiation with an active energy beam and the like.

The resin composition of the present invention thus cured with crosslinking can be decomposed by bringing it into contact with an aqueous solution of formic acid, acetic acid, p-toluenesulfonic acid, dodecylbenzenesulfonic acid, sulfuric acid, phosphoric acid or the like, and further with a]

[solution containing an organic solvent, and thereby the cured composition can be removed.

Examples

The following will explained the present invention in detail with reference to the examples.

Examples 1 to 4

Two hundred parts by weight of DENACOL EX-841 (an epoxydated polyethylene resin manufactured by Nagase Chemicals Ltd.), 200 parts by weight of N-methylpyrrolidone and 84 parts by weight of iminodiacetic acid dihydrazide were mixed and reacted at 100°C for 4 hours to obtain slightly colored highly viscous liquid. To the solution was added 177 parts by weight of diacetone acryl amide and 0.3 parts by weight of SUMILIZER BHT (a polymerization inhibitor manufactured by Sumitomo Chemical Co., Ltd.). The mixture was stirred for a long period of time and then stored as it was.

A phtoinitiator, IRGACURE (manufactured by Ciba specialty Chemicals Corp.) was incorporated into the solution in an amount of 3% and the resin was cured by UV irradiation. Table 1 shows curing conditions, test results of coating properties, and re-dissolving time.]

[Table 1

	Example 1	Example 2	Example 3	Example 4
Added monomer species	None	None	i-BMA	P-FA2
Added amount (resin/monomer)	-	-	2/1	2/1
Exposure dose (mmJoule/cm ²)	300	1500	3000	1500
Film thickness (μm)	20	15	12	18
Pencil hardness	H	H	H	HB
Adhesiveness	100/100	100/100	100/100	100/100
Impact resistance (1/2 φ, 1kg)	50<	50<	50<	50<
Acetone resistance *	No change	No change	No change	No change
Re-dissolving property (minute) **	1.5	3.5	1	5

(Notes)

* : The appearance of the coating was observed after one drop of acetone was placed on the coating and then evaporated.

** : The coating was immersed in a coating-dissolving solution of toluene/isopropyl alcohol/water/p-toluenesulfonic acid = 42/45/10/3, and the time for dissolution of the coating was measured.

10 i-BMA: isobutyl methacrylate

P-FA2: PLACCEL FA2 (a functional monomer manufactured by Daicel Chemical Industries Ltd.)

Examples 5 to 7

After 208.8 parts by weight of adipic acid
 15 dihydrazide and 278.4 parts by weight of diacetone alcohol was mixed, the mixture was subjected to dehydration under heating at 120°C for 15 hours to obtain an adduct of adipic]

[acid dihydrazide and diacetone alcohol. The product was isolated by dissolving it into 360 parts by weight of N-methylpyrrolidone.

The concentration of solid mass of the adduct solution was about 60%. A 200 parts by weight portion of the solution was heated to 80°C and, after the addition of one drop of dibutyltin dilaurate, 37 parts by weight of tolylene diisocyanate (TDI) was added dropwise over a period of one hour, followed by the maintenance at that temperature for further 4 hours. The absence of isocyanate group was confirmed on IR measurement.

To 10 parts by weight of the solution was added 1 part by weight of SUMIDUR N3500 (manufactured by Sumitomo Bayer Urethane Co., Ltd.). The resulting solution was painted on a plate treated with zinc phosphate by means of a bar coater and dried according to the method shown in Table 2. Table 2 also shows coating properties and re-dissolving property.]

[Table 2]

	Example 5	Example 6	Example 7
Drying conditions	drying at room temperature for 7 days	drying at 60°C for 30 minutes then at room temperature for 7 days	drying at 120°C for 30 minutes then at room temperature for 7 days
Film thickness (μm)	23	22	26
Pencil hardness	H	H	3H
Adhesiveness on latticecut test	100/100	100/100	100/100
Impact resistance (1/2 φ, 1kg)	10 cm	10 cm	10 cm
Water resistance (immersing in water for 7 days)	No change	No change	No change
Re-dissolving property (minute) *	2	20	30

(Note)

* : The time for dissolution of the coating when it was immersed in a solution of N-methylpyrrolidone/water/p-toluenesulfonic acid = 78/10/3 at 60°C.

The curable composition of the present invention can be easily decomposed by an aqueous solution of formic acid or the like or the solution additionally containing an organic solvent, and therefore serves an excellent effect that it is easy to recycle the materials to which the composition are attached.

Although only some exemplary embodiments of this invention have been described in detail above, those skilled]

[in the art will readily appreciated that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention.]

Technical Field of the Invention

The present invention relates to a cold setting coating composition capable of forming an elastic coated film excellent in weathering resistance and water resistance using an oxidatively curable urethane-modified vinyl resin.

Background of the Invention

Hitherto, an alkyd resin using an unsaturated fatty acid is well known as a cold setting resin for coating which is stable in a solution state for a long period of time, and is widely used as a coating for inside and outside of a building. However, the alkyd resin tends to cause weather-deterioration by ultraviolet ray, so that its performance is insufficient for outdoor use. As measures for solving the problem of weathering resistance, for example, a fatty acid-modified acrylic resin has been proposed in British patent No. 793,776, and a non-aqueous dispersion-type acrylic resin obtained by dispersion polymerization in the presence of the fatty acid-modified acrylic resin has been proposed in Japanese Patent Publication No. 3-71448/1991. However, in the case of fatty acid-modified acrylic resin, the weathering resistance was improved a little but the coating performances such as weathering resistance, water resistance and acid and alkali resistances were still not satisfactory. Furthermore,

in the case of the above non-aqueous dispersion-type acrylic resin, secondary particles having a large particle size formed during the production reaction, so that it was impossible to obtain a stable dispersion having a narrow
5 particle size distribution and the gloss of coated film is also insufficient.

In Japanese Patent Publication No. 52-26260/1977, there has been proposed a non-aqueous dispersion-type acrylic resin produced by dispersion polymerization in the presence
10 of an acrylic resin where a vinyl monomer having an oxidatively curable unsaturated group is used as a copolymerizing component. In this case, a stable non-aqueous dispersion could be obtained and it was possible to form a coated film excellent in water resistance, acid resistance,
15 alkali resistance and the like, but there existed a problem that the initial dryness of coated film is insufficient.

Summary of the Invention

An object of this invention is to improve weathering resistance and water resistance of a coated film made from a
20 cold setting coating composition of the present invention. Another object of the present invention is to improve crack-following ability of the undercoat. For these purposes, the cold setting coating composition of the present invention contains an urethane-modified vinyl resin (A) as a film-
25 forming component. The resin (A) is produced by reacting a reaction product with an isocyanate group-possessing compound (c). The reaction product is made by reacting an epoxy group-containing vinyl copolymer (a), which is a copolymer of a polymerizable unsaturated monomer containing an epoxy group,

with another polymerizable unsaturated monomer capable of polymerizing with said monomer, and a fatty acid component (b) containing an unsaturated fatty acid. The epoxy group-containing vinyl copolymer (a) may be produced by copolymerizing 3 to 70% by weight of the polymerizable unsaturated monomer containing an epoxy group with 30 to 97% by weight of the other polymerizable unsaturated monomer. The epoxy group-containing vinyl copolymer (a) may have a number average molecular weight of 1,000 to 100,000 and a glass transition temperature of 0 to 100°C. The fatty acid component (b) containing an unsaturated fatty acid may have an iodine value of 50 to 200. The ratio of the fatty acid component (b) containing an unsaturated fatty acid may be from 1 to 60 parts by weight based on 100 parts by weight of the epoxy group-containing vinyl copolymer (a). An equivalent ratio of the isocyanate group to the hydroxyl group in the fatty acid-modified copolymer (NCO/OH) may be from 0.05 to 2.0.

In addition to the resin (A), the cold setting coating composition of the present invention may further contain a polymer-dispersion (B) obtained by polymerizing, in an organic liquid in which vinyl monomers are soluble and the polymer formed from the monomers are insoluble, two or more of the vinyl monomers in the presence of a dispersion stabilizer (d) which is soluble in the organic liquid, in amounts of 10 to 90% by weight of (A) and 90 to 10% by weight of (B) based on total solid matter weight of both of them. The dispersion stabilizer (d) may be a resin having an oxidatively polymerizable double bond. The resin having an

oxidatively polymerizable double bond may be a resin obtained by copolymerizing a vinyl monomer having an oxidatively polymerizable double bond and another vinyl monomer.

Preferred Embodiments of the Invention

5 The present invention, the urethane-modified vinyl resin (A) is an oxidatively curable resin produced by further reacting, with an isocyanate group-possessing compound (c), a reaction product between an epoxy group-containing vinyl copolymer (a) and a fatty acid component (b) containing an
10 unsaturated fatty acid.

The example of the polymerizable unsaturated monomer containing an epoxy group which is a copolymerizing component of the above epoxy group-containing vinyl copolymer (a) include glycidyl (meth)acrylate, β -methylglycidyl
15 (meth)acrylate, 3,4-epoxycyclohexylmethyl (meth)acrylate, 3,4-epoxycyclohexylpropyl (meth)acrylate, allyl glycidyl ether, and the like.

The examples of the other polymerizable unsaturated monomer include acrylic or methacrylic acid esters of alkyl
20 or cycloalkyl having 1 to 24 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, decyl (meth)acrylate, lauryl (meth)acrylate,
25 stearyl (meth)acrylate, cyclohexyl (meth)acrylate, isobornyl (meth)acrylate; hydroxyl group-containing monomers including hydroalkyl esters of α,β -ethylenically unsaturated carboxylic acids such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-

hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate
and 4-hydroxybutyl (meth)acrylate, and α,β -ethylenically
unsaturated carboxylic acid esters having an alkylene oxide
chain and hydroxyl group such as polyethylene glycol
5 mono(meth)acrylate, polypropylene glycol mono(meth)acrylate;
1,2,2,6,6-pentamethylpiperidyl (meth)acrylate, 2,2,6,6-
tetramethylpiperidiny (meth)acrylate, 2-(2'-hydroxy-5'-
methacryloxyphenyl)-2H-benzotriazole, styrene, vinyl acetate,
and the like.

10 In the epoxy group-containing vinyl copolymer (a),
it is suitable that the copolymerization ratio between the
polymerizable unsaturated monomer containing an epoxy group
and the above other polymerizable unsaturated monomer usually
ranges 3 to 70% by weight, preferably 10 to 50% by weight for
15 the polymerizable unsaturated monomer containing an epoxy
group, and 30 to 97% by weight, preferably 50 to 90% by
weight for the above other polymerizable unsaturated monomer
in view of the reactivity for addition at the reaction with
the unsaturated fatty acid (b) and the solubility of the
20 resulting epoxy group-containing vinyl copolymer (a) in a
solvent.

In the epoxy group-containing vinyl copolymer (a),
when a hydroxyl group-containing monomer is used, the monomer
is used in an amount so that gelation does not occur during
25 the reaction with the polyisocyanate compound (c). Usually,
it is suitable to use the hydroxyl group-containing monomer
in an amount of 30% by weight or less among the monomer
components constituting the vinyl copolymer (a).

The method of copolymerization for obtaining the

above epoxy group-containing vinyl copolymer (a) is not particularly limited but solution polymerization which is carried out in an organic solvent in the presence of a radical polymerization initiator is preferable from the viewpoint of the easiness of the reaction with the fatty acid component (b) and the isocyanate group-possessing compound (c).

The examples of the radical polymerization initiator to be used for the synthesis of the above epoxy group-containing vinyl copolymer (a) by solution polymerization include azo-type polymerization initiators such as 2,2'-azobisisobutyronitrile and 2,2'-azobis(2,4-dimethylvaleronitrile); peroxide-type polymerization initiators such as lauryl peroxide, t-butyl peroxy-2-ethylhexanoate and benzoyl peroxide. The examples of the organic solvent for the synthesis by solution polymerization include aliphatic hydrocarbon-type solvents such as n-hexane, n-octane, 2,2,2-trimethylpentane, isooctane, n-nonane, cyclohexane and methylcyclohexane; aromatic hydrocarbon-type solvents such as benzene, toluene, xylene and ethylbenzene; petroleum-type solvents such as mineral spirit, "Swasol 1000" (a product of Cosmo Oil Co., Ltd.), petroleum ether, petroleum benzine and petroleum naphtha; ketone-type solvents such as methyl isobutyl ketone; ester-type solvents such as isobutyl acetate; alcohol-type solvents such as isopropanol, and these can be optionally used solely or in combination of two or more according to necessity.

The above epoxy group-containing vinyl copolymer (a) preferably has a number average molecular weight in the range

of 1,000 to 100,000, particularly 2,000 to 70,000 and a glass transition temperature (Tg) in the range of 0 to 100°C in view of the physical properties of the resulting coated film and quick drying ability.

5 The above fatty acid component (b) is a fatty acid component necessarily containing an unsaturated fatty acid and optionally containing a saturated fatty acid, and is suitably has an iodine value in the range of about 50 to 200. When the iodine value is less than about 50, the curability
10 of the coated film decreases, while there is a possibility of gelation during the production of the resin when the iodine value exceeds about 200. Thus, both cases are not preferred.

The representative examples of the unsaturated fatty acid which is a necessary component of the fatty acid
15 component (b) include fish oil fatty acids, dehydrated castor oil fatty acids, safflower oil, linseed oil fatty acids, soybean oil fatty acids, sesame oil fatty acids, poppy seed oil fatty acids, perilla oil fatty acids, hempseed oil fatty acids, grape seed oil fatty acids, corn oil fatty acids, tall
20 oil fatty acids, sunflower oil fatty acids, cotton seed oil fatty acids, walnut oil fatty acids, rubberseed oil fatty acids, and the like. The unsaturated fatty acid is a fatty acid having an oxidatively curable polymerizable unsaturated group, and imparts oxidative curability to the urethane-
25 modified vinyl resin in the present invention.

The examples of the saturated fatty acid which the fatty acid component (b) may contain in addition to the above unsaturated fatty acid according to necessity include non-drying oil fatty acids such as coconut oil fatty acids,

hydrogenated coconut oil fatty acids and palm oil fatty acids; caproic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and the like.

The ratio of the fatty acid component (b) to be used is preferably from 1 to 60 parts by weight, preferably 5 to 30 parts by weight based on 100 parts by weight of the resin solid matter of the above epoxy group-containing vinyl copolymer (a) in view of the curability and weathering resistance of the resulting coated film.

In the present invention, the reaction between the epoxy group-containing vinyl copolymer (a) and the fatty acid component (b) is based on esterification of the epoxy group in the copolymer (a) with the carboxyl group in the fatty acid component (b), and a secondary hydroxyl group is usually formed by the reaction. At the reaction, there may be used a reaction catalyst including a tertiary amine such as N,N-dimethylaminoethanol; a quaternary ammonium salt such as tetrabutylammonium bromide; and the like. In the case of using the reaction catalyst, the amount to be used is suitably in the range of 0.01 to 100 parts by weight based on the total amount of the copolymer (a) and the fatty acid component (b).

The conditions for the reaction of the copolymer (a) and the fatty acid component (b) may be any of the conditions under which the epoxy group in the copolymer (a) can be reacted with the carboxyl group in the fatty acid component (b) without occurring problems at the reaction such as gelation, and the conditions of heating at about 100 to 170°C for about 2 to 10 hours may be usually suitable.

The examples of the isocyanate group-possessing compound (c) to be reacted with the fatty acid-modified copolymer produced as above include aromatic, alicyclic or aliphatic polyisocyanate compounds such as tolylene diisocyanate, xylylene diisocyanate, phenylene diisocyanate, diphenylmethane diisocyanate, bis(isocyanatemethyl) cyclohexane, tetramethylene diisocyanate, hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, methylene diisocyanate and isophorone diisocyanate; and isocyanurate compounds or biuret compounds thereof; terminal isocyanate-containing compounds produced by reacting an excess amount of these polyisocyanate compounds with a low molecular weight compound containing an active hydrogen such as ethylene glycol, propylene glycol, trimethylolpropane, hexanetriol or castor oil; lysine triisocyanate and the like.

The amount of the above isocyanate group-possessing compound (c) to be used may be determined so that the equivalent ratio (NCO/OH) of the isocyanate group in the isocyanate group-possessing compound (c) to the hydroxyl group in the fatty acid-modified copolymer becomes from 0.05 to 2.0, preferably from 0.1 to 1.2 in view of weathering resistance and physical properties of the coated film to be formed.

At the reaction of the above isocyanate group-possessing compound (c) with the fatty acid-modified copolymer produced by the reaction between (a) and (b), in the case that the viscosity of the reaction system exceeds the suitable range by its increase with the proceeding of the reaction, for example, the reaction can be controlled by

adding suitable amount of an alcohol, an phenol, a lactam, an oxime or the like.

The reaction of the above fatty acid-modified copolymer with the isocyanate group-possessing compound (c) may be carried out in the presence of a reaction catalyst, if necessary. The above reaction is based on the reaction between the hydroxyl groups in the fatty acid-modified copolymer and the isocyanate groups in the isocyanate group-possessing compound (c). The hydroxyl groups in the above fatty acid-modified copolymer may be the hydroxyl groups originally present in the copolymer (a) and the hydroxyl groups formed by the reaction of the copolymer (a) and the fatty acid component (b).

The examples of the above reaction catalyst include organometallic compounds such as dibutyltin bis(acetylacetonate), dibutyltin diacetate, dibutyltin di(2-ethylhexylate), dibenzyltin di(2-ethylhexylate), dibutyltin dilaurate, dibutyltin diisocylmaleate and tetrabutyl titanate. These reaction catalysts may be used solely or in combination of two or more.

The above reaction catalyst is suitably used in an amount of 0.001 to 5 parts by weight, preferably 0.005 to 1 part by weight based on 100 parts by weight of total amount of the fatty acid-modified copolymer and the isocyanate group-possessing compound (c) in view of the accelerating effect of the reaction.

The coating composition of the present invention contains the above urethane-modified vinyl resin as a film-forming component, and may also contain, as a film-forming

component to be used in combination with the above vinyl resin, a polymer dispersion (B) produced by polymerizing two or more of vinyl monomers in an organic liquid in which the vinyl monomers are soluble and the polymer formed from the monomers are insoluble, in the presence of a dispersion stabilizer (d) which is soluble in the organic liquid.

The above polymer dispersion (B) is obtained by polymerizing two or more of the vinyl monomers in an organic liquid in which vinyl monomers are soluble and the polymer formed from the monomers are insoluble, in the presence of a dispersion stabilizer (d) which is soluble in the organic liquid.

The examples of the above organic liquid include aliphatic hydrocarbon-type solvents such as n-hexane, n-octane, 2,2,2-trimethylpentane, isooctane, n-nonane, cyclohexane and methylcyclohexane; petroleum-type solvents such as mineral spirit, "SWAZOLE 1000" (a product of Cosmo Oil Co., Ltd.), petroleum ether, petroleum benzine and petroleum naphtha; and the like, and these may be used solely or in combination of two or more. In combination with these solvents, there may be used aromatic hydrocarbon-type solvents such as benzene, toluene, xylene and ethylbenzene; ketone-type solvents such as methyl isobutyl ketone; ester-type solvents such as isobutyl acetate; alcohol-type solvents such as isopropanol; and the like according to necessity.

As the dispersion stabilizer (d) soluble in the above organic solvent, various kinds of hitherto known resins can be used and usually a resin having a number average molecular weight of about 1,000 to 100,000 is used.

Particularly, as the dispersion stabilizer (d), a resin having an oxidatively polymerizable double bond is preferable in view of the curability of the coated film to be formed.

The resin having an oxidatively polymerizable double bond is usually a resin obtained by radical copolymerization of 5 to 70% by weight, preferably 15 to 50% by weight of a vinyl monomer having an oxidatively polymerizable double bond and 30 to 95% by weight, preferably 50 to 85% by weight of the other vinyl monomer in the above organic solvent in the presence of radical polymerization initiator. When the amount of the vinyl monomer having an oxidatively polymerizable double bond in the copolymer is too small, there is a possibility that sufficient curing cannot be attained especially at early stage of the film formation. On the other hand, when the amount is too large, there is a possibility that unreacted monomer may remain. Thus, both cases are undesirable.

The examples of the vinyl monomer having an oxidatively polymerizable double bond include

dicyclopentadiene derivatives such as dihydrodicyclopentadiene mono(meth)acrylate, dihydrodicyclopentadieneethyl mono(meth)acrylate and dihydrodicyclopentadiene monoallyl ether.

The examples of other vinyl monomers include styrene, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, decyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl

(meth)acrylate, isobornyl (meth)acrylate, (meth)acrylic acid, 2-hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate and the like, and these may be used solely or in combination of two or more.

5 The examples of the above radical polymerization initiator include azo-type polymerization initiators such as 2,2'-azobisisobutyronitrile and 2,2'-azobis(2,4-dimethylvaleronitrile); peroxide-type polymerization initiator such as lauryl peroxide, t-butyl peroxy-2-ethylhexanoate and benzoyl peroxide.

10 The examples of the vinyl monomer to be polymerized in the presence of the dispersion stabilizer (d) obtained as above include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, (meth)acrylonitrile, 2-methoxyethyl (meth)acrylate, 2-methoxybutyl (meth)acrylate, (meth)acrylamide, vinylpyrrolidone, (meth)acrylic acid, maleic acid, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, glycidyl (meth)acrylate, styrene, vinyltoluene, α -methylstyrene and vinyl acetate, and these may be used solely or in combination of two or more.

25 In view of the balance of elasticity and strain resistance, a multivinyl compound may be used in an amount of 2% by weight or less as the above vinyl monomer. The examples of the multivinyl compound include polymerizable unsaturated monocarboxylic acid esters of a polyhydric

alcohol, polymerizable unsaturated alcohol esters of a
polybasic acid and aromatic compounds substituted by two or
more of vinyl groups, more specifically allyl (meth)acrylate,
dipropyleneglycol di(meth)acrylate, 1,6-hexandiol
5 di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 2-
propenyl (meth)acrylate, 1,1,1-trishydroxymethylethane
di(meth)acrylate, triallylisocyanurate, divinylbenzene and
the like.

The above dispersion polymerization is carried out
10 in the above organic liquid in the presence of a radical
polymerization initiator. As the radical polymerization
initiator, the same ones as mentioned above can be used.

The polymer dispersion (B) obtained as above is a
stable dispersion of the particles having a light intensity
15 average particle size of 150 to 900 nm, mostly about 250 to
400 nm according to dynamic light scattering.

The coating composition of the present invention may
contain additives for coating such as an oxidative curing
reaction catalyst, a pigment, an organic solvent, an
20 ultraviolet absorber, a light stabilizer, a surface
controller, a pigment dispersant, a rheology controller, a
skin-forming inhibitor of coating liquid, an antiseptic agent,
antialgae agent, a plasticizer, an antifoaming agent and the
like according to necessity.

25 The examples of the above oxidative curing reaction
catalyst include organometallic compounds such as cobalt
octylate, cobalt naphthenate, manganese octylate, manganese
naphthenate, zirconium octylate and zirconium naphthenate.
In addition, a compound activating catalytic action such as

1,10-phenanthroline may be used in combination with the
oxidative curing reaction catalyst.

The examples of the rheology controller include
thickening agents such as polyethylene oxide and a fatty acid
amide wax, and alkoxysilyl compounds or condensates thereof,
and these may be used solely or in combination of two or more.

The coated film obtained from the composition of the
present invention has very good appearance such as surface
gloss and is excellent in weathering resistance, chemical
resistance and alkali resistance, as well as, in the presence
of oxidative curing reaction catalyst, the composition can be
cured within several hours after the coating and shows
excellent cold setting ability.

The coating composition of the present invention is
applicable to the surfaces of materials such as metal, slate
and mortar, undercoat (e.g., sealing material, primer,
thickness-main material) surfaces thereof, or old coated
surfaces, and is useful especially for inorganic building
materials such as slate and mortar and for coated surfaces
thereof having elasticity.

Examples

The following will explain the present invention in
detail with reference to Examples. "part(s)" and "%" means
"part(s) by weight" and "% by weight", respectively.

Production of Urethane-Modified Vinyl Resin Solutions Production Example 1

Into a flask was charged 100 parts of mineral spirit,
followed by the elevation of temperature to 115°C under
stirring with introducing nitrogen gas. Then, the below-

described mixture of monomers and other compound were added dropwise thereto over a period of 4 hours with maintaining the temperature at 115°C.

	<u>styrene</u>	<u>20 parts</u>
5	<u>n-butyl methacrylate</u>	<u>25 parts</u>
	<u>i-butyl methacrylate</u>	<u>10 parts</u>
	<u>2-ethylhexyl acrylate</u>	<u>25 parts</u>
	<u>glycidyl methacrylate</u>	<u>20 parts</u>
	<u>2,2'-azobisisobutyronitrile</u>	<u>1 part</u>

10 Then, after aging at 115°C for 2 hours and then the temperature was elevated to 140°C, 30 parts of linseed oil fatty acids and 0.4 part of N,N-dimethylaminoethanol as the reaction catalyst were added thereto, and the mixture was maintained at 160°C for 5 hours to carry out the addition of
15 the fatty acids. The resin acid value was traced by KOH titration method and the end point was determined as the time point at which the resin acid value was decreased to 1.0 or lower. After the completion of the reaction, the mixture was diluted by adding 45 parts of xylene to obtain a brown clear
20 viscous fatty acid-modified copolymer solution (a-1), 50% of which was nonvolatile matter.

The fatty acid-modified copolymer solution (a-1) was cooled to 100°C, and 5 parts of "Desmodur H" (manufactured by Sumitomo Bayer Urethane Co., Ltd., hexamethylene
25 diisocyanate), 14 parts of mineral spirit, 6 parts of xylene and 0.05 part of dibutyltin dilaurate as a reaction catalyst were added therein. Then, the whole was reacted at the same temperature for 2 hours to obtain a brown clear viscous urethane-modified vinyl resin solution (A-1), about 45% of

which was nonvolatile matter.

Production Example 2

To 275 parts of 50% fatty acid-modified copolymer solution (a-1) obtained in Production Example 1 were added 12 parts of "TPA-100" (manufactured by Asahi Chemical Co., Ltd., isocyanurate of hexamethylene diisocyanate), 30 parts of xylene and 0.05 part of dibutyltin dilaurate as a reaction catalyst, and the whole was reacted for 1 hour with maintaining the temperature at 100°C. Then, 2 parts of n-butyl alcohol was added thereto and the mixture was further reacted for 1 hour to obtain a brown clear viscous urethane-modified vinyl resin solution (A-2), about 45% of which was nonvolatile matter.

Production Example 3

To 275 parts of the 50% fatty acid-modified copolymer solution (a-1) obtained in Production Example 1 were added 23 parts of "TSE-100" (manufactured by Asahi Chemical Co., Ltd., the one obtained by modifying isocyanurate of hexamethylene diisocyanate to soft-type), 30 parts of mineral spirit, 15 parts of xylene and 0.05 part of dibutyltin dilaurate as a reaction catalyst, and the whole was reacted for 1 hour with maintaining the temperature at 100°C. Then, 2 parts of n-butyl alcohol was added thereto and the mixture was further reacted for 1 hour to obtain a brown clear viscous urethane-modified vinyl resin solution (A-3), about 45% of which was nonvolatile matter.

Production Example 4

Into a flask was charged 100 parts of mineral spirit, followed by the elevation of temperature to 115°C under

stirring with introducing nitrogen gas. Then, the below-
described mixture of monomers and other compound were added
dropwise thereto over a period of 4 hours with maintaining
the temperature at 115°C.

5	<u>styrene</u>	<u>15 parts</u>
	<u>n-butyl methacrylate</u>	<u>25 parts</u>
	<u>i-butyl methacrylate</u>	<u>10 parts</u>
	<u>2-ethylhexyl acrylate</u>	<u>25 parts</u>
	<u>glycidyl methacrylate</u>	<u>20 parts</u>
10	<u>"RUVA-093" (Note 1)</u>	<u>5 parts</u>
	<u>2,2'-azobisisobutyronitrile</u>	<u>1 part</u>

Then, after aging at 115°C for 2 hours and then the
temperature was elevated to 140°C, 30 parts of linseed oil
fatty acids and 0.4 part of N,N-dimethylaminoethanol as a
15 reaction catalyst were added thereto, and the mixture was
maintained at 160°C for 5 hours to carry out the addition of
the fatty acids. The resin acid value was traced by KOH
titration method and the end point was determined as the time
point at which the resin acid value was decreased to 1.0 or
20 lower. After the completion of the reaction, the mixture was
diluted by adding 45 parts of xylene to obtain a brown clear
viscous fatty acid-modified copolymer solution (a-2), 50% of
which was nonvolatile matter.

The fatty acid-modified copolymer solution (a-2) was
25 cooled to 100°C, and 5 parts of "DESMODUR H" (manufactured by
Sumitomo Bayer Urethane Co., Ltd., hexamethylene
diisocyanate), 14 parts of mineral spirit, 6 parts of xylene
and 0.05 part of dibutyltin dilaurate as a reaction catalyst
were added therein. Then, the whole was reacted at the same

temperature for 2 hours to obtain a brown clear viscous urethane-modified vinyl resin solution (A-4), about 45% of which was nonvolatile matter.

(Note 1) "RUVA-093": manufactured by Otsuka Chemical Co.,

5 Ltd., 2-(2'-hydroxy-5'-methacryloxyphenyl)-2H-benzotriazole
Production Example 5

Into a flask was charged 100 parts of mineral spirit,
followed by the elevation of temperature to 115°C under
stirring with introducing nitrogen gas. Then, the mixture
10 of:

	<u>styrene</u>	<u>25 parts</u>
	<u>n-butyl methacrylate</u>	<u>14 parts</u>
	<u>i-butyl methacrylate</u>	<u>16 parts</u>
	<u>2-ethylhexyl acrylate</u>	<u>18 parts</u>
15	<u>glycidyl methacrylate</u>	<u>27 parts</u>
	<u>2,2'-azobisisobutyronitrile</u>	<u>1 part</u>

was added dropwise thereto over a period of 4 hours with
maintaining the temperature at 115°C. Then, after aging at
115°C for 2 hours and then the temperature was elevated to
20 140°C, 43 parts of soybean oil fatty acids and 0.4 part of
N,N-dimethylaminoethanol as a reaction catalyst were added
thereto to carry out the addition of the fatty acids. The
resin acid value was traced by KOH titration method and the
end point was determined as the time point at which the resin
25 acid value was decreased to 1.0 or lower. After the
completion of the reaction, the mixture was diluted by adding
45 parts of mineral spirit and the temperature was lowered to
120°C. Then, 6.7 parts of hexamethylene diisocyanate was
added thereto and the mixture was reacted at the same

temperature for 1 hour to obtain a brown clear urethane-
modified vinyl resin solution (A-5), 51% of which was
nonvolatile matter.

Production Example 6

5 A brown clear urethane-modified vinyl resin solution
(A-6), 51% of which was nonvolatile matter, was obtained in a
similar manner to Production Example 5 with the exception
that the unsaturated fatty acids to be used for the
production of the urethane-modified vinyl resin solution was
10 changed from soybean oil fatty acids in Production Example 5
to linseed oil fatty acids.

Production Example 7

Into a flask was charged 53 parts of mineral spirit,
followed by the elevation of temperature to 115°C under
15 stirring with introducing nitrogen gas. Then, the mixture
of:

	<u>styrene</u>	<u>25 parts</u>
	<u>n-butyl methacrylate</u>	<u>14 parts</u>
	<u>i-butyl methacrylate</u>	<u>16 parts</u>
20	<u>2-ethylhexyl acrylate</u>	<u>18 parts</u>
	<u>2-hydroxyethyl methacrylate</u>	<u>27 parts</u>
	<u>2,2'-azobisisobutyronitrile</u>	<u>1 part</u>

was added dropwise thereto over a period of 4 hours with
maintaining the temperature at 115°C. Then, the mixture was
25 aged at 115°C for 2 hours to obtain a colorless clear acrylic
resin solution, 65% of which was nonvolatile matter. Then,
154 parts of the acrylic resin solution, 43 parts of soybean
oil fatty acids and 24 parts of xylene were charged to a
reaction apparatus fitted with a thermometer, a stirrer, a

heating device and a rectifying tower, and the temperature
was elevated under stirring with introducing nitrogen gas.
The esterification of the hydroxyl groups in the acrylic acid
resin backbone with the fatty acids was carried out under
5 xylene reflux at a reaction temperature of 170°C with
removing the water formed during the condensation. The resin
acid value was traced by KOH titration method and the end
point was determined as the time point at which the resin
acid value was decreased to 1.0 or lower. After the
10 completion of the reaction, the mixture was diluted by adding
65 parts of mineral spirit and the temperature was lowered to
120°C. Then, 6.7 parts of hexamethylene diisocyanate was
added thereto and the mixture was reacted at the same
temperature for 1 hour to obtain a brown clear urethane-
15 modified vinyl resin solution (A-7), 51% of which was
nonvolatile matter.

Production Example 8

An urethane-modified vinyl resin solution (A-8) was
obtained in a similar manner to Production Example 5 with the
20 exception that 6.7 parts of the hexamethylene diisocyanate to
be used for the production of the urethane-modified vinyl
resin solution in Production Example 5 was changed to 73.4
parts of the urethane derivative produced in the following
step (Note 2).

25 (Note 2) Into a flask were charged 600 parts of methyl ethyl
ketone and 900 parts of polypropylene glycol having an
average molecular weight of 900, followed by the elevation of
temperature to 50°C under stirring with introducing nitrogen
gas. Then, 336 parts of hexamethylene diisocyanate was added

dropwise therein over a period of about 30 minutes. At that time, when the reaction temperature was elevated to 80°C, the temperature was maintained at 80°C by controlling the addition rate or cooling. After the completion of the addition, the whole was reacted at the same temperature for 2 hours to obtain an urethane derivative having isocyanate groups at both ends.

Production of Polymer Dispersions

Production Example 9

Into a flask was charged 80 parts of mineral spirit (manufactured by Nippon Oil Company, Ltd., "NISSEKI A SOLVENT"), followed by the elevation of temperature to 110°C under stirring with introducing nitrogen gas. Then, the mixture of:

styrene	25 parts
n-butyl methacrylate	12 parts
i-butyl methacrylate	43 parts
2-ethylhexyl acrylate	20 parts
2,2'-azobisisobutyronitrile	1.5 parts

was added dropwise thereto over a period of 4 hours with maintaining the temperature at 110°C. Then, after the temperature was elevated to 120°C, the mixture was aged for 2 hours to obtain an almost colorless clear viscous acrylic resin solution, 55% of which was nonvolatile matter. This solution was used as a dispersion stabilizer.

Into a flask were charged 185.4 parts of the dispersion stabilizer produced in the above, 25.5 parts of isobutyl acetate and 101 parts of mineral spirit, followed by the elevation of temperature to 100°C under stirring with

introducing nitrogen gas. Then, a mixture of:

	<u>methyl methacrylate</u>	<u>25 parts</u>
	<u>ethyl acrylate</u>	<u>15 parts</u>
	<u>methyl acrylate</u>	<u>40 parts</u>
5	<u>2-hydroxyethyl acrylate</u>	<u>20 parts</u>
	<u>2,2'-azobisisobutyronitrile</u>	<u>1.5 part</u>

was added dropwise thereto over a period of 3 hours with
maintaining the temperature at 100°C. Then, the mixture was
aged at 100°C for 3 hours to obtain a milky-white polymer
10 dispersion (B-1), 50% of which was nonvolatile matter. A
light intensity average particle size according to dynamic
light scattering (hereinafter, simply referred to as
"particle size") was 370 nm.

Production Example 10

15 A milky-white polymer dispersion (B-2) was obtained
in a similar manner to Production Example 9 with the
exception that the following mixture was used as a monomer
mixture to be used for the production of a dispersion
stabilizer for polymer dispersion. The particle size was 350
20 nm.

	<u>FANCRYL FA-512MT (Note 3)</u>	<u>10 parts</u>
	<u>styrene</u>	<u>25 parts</u>
	<u>n-butyl methacrylate</u>	<u>12 parts</u>
	<u>i-butyl methacrylate</u>	<u>33 parts</u>
25	<u>2-ethylhexyl acrylate</u>	<u>20 parts</u>
	<u>2,2'-azobisisobutyronitrile</u>	<u>1 part</u>

(Note 3) "FANCRYL FA-512MT": manufactured by Hitachi
Chemical Co., Ltd., an oxidatively curable monomer

Production Example 11

A milky-white polymer dispersion (B-3) was obtained in a similar manner to Production Example 9 with the exception that the following mixture was used as a monomer mixture to be used for the production of a dispersion stabilizer for polymer dispersion. The particle size was 320 nm.

FANCRYL FA-512MT (Note 3)	40 parts
styrene	15 parts
n-butyl methacrylate	12 parts
i-butyl methacrylate	23 parts
2-ethylhexyl acrylate	20 parts
2,2'-azobisisobutyronitrile	1.5 parts

Preparation of Coating Composition

Examples 1 to 4 and Comparative Example 1

Using each of the 45% urethane-modified vinyl resin solutions obtained in the above Production Examples, each cold setting coating composition was obtained by adding each component at the mixing composition shown in Table 1 (shown by solid matters) to an one-litter volume mayonnaise bottle together with 250 parts of glass beads having a diameter of 2 mm, stirring at a paint shaker for 2 hours to form a pigment paste, adding the above 45% urethane-modified vinyl resin solution as well as cobalt naphthenate and lead naphthenate as shown in the table, stirring the whole to form a homogeneous mixture, and removing the glass beads. By the way, in Comparative Example 1, the fatty acid-modified copolymer solution (a-1) was used instead of the urethane-modified vinyl resin solution.

Performance Tests

Upon each of the cold setting coating compositions obtained in the above examples 1 to 4 and Comparative Example 1, various tests were carried out according to the following test methods. The test results were shown in following Table 1.

Test Methods

(*1) Initial dryness: After a glass plate was coated with each cold setting coating composition by means of a 300 μ m applicator, the finger-contact dryness of the coated film after standing at 20°C under 70% RH for 6 hours was determined and evaluated according to the following standard.

◎: No fingerprint is marked.

○: Slight fingerprint is marked.

△: Fingerprint is marked.

×: ?The coated film adheres to finger.

(*2) Gloss of the coated film: After a glass plate was coated with each cold setting coating composition by means of a 300 μ m applicator, a 60° specular reflection rate of the coated film after drying in a room at 20°C under 70% RH for 1 week was determined and evaluated according to the following standard.

◎: 90% or more

○: from 80% to less than 90%

△: from 70% to less than 80%

×: less than 70%

(*3) Weathering resistance: After a slate plate coated with "ALES RETAN" (manufactured by Kansai Paint Co., Ltd., a white glossy coating) was coated with each cold setting coating composition by means of a 300 μ m applicator and the whole was

dried in a room at 20°C under 70% RH for 1 week, gloss-
retaining rate was evaluated after exposure to sunshine
wetherometer for 1500 hours.

◎: 90% or more

5 ○: from 80% to less than 90%

△: from 70% to less than 80%

×: less than 70%

10 (*4) Water resistance: After a slate plate was coated with
each cold setting coating composition by means of a 300 µm
applicator and the whole was dried in a room at 20°C under
70% RH for 1 week, the state of the coated film after
immersing the coated plate in a tap water (20°C) for 3 days
was observed and evaluated according to the following
standard.

15 ○: No change

△: Slight swelling is observed.

×: Remarkable swelling is observed.

20 (*5) Acid resistance: On the coated plate obtained as in
(*1) was added dropwise 0.5 cc of 0.1N sulfuric acid aqueous
solution, and after standing at 20°C for 24 hours, the state
of the coated plate after washing with water was observed.

○: No change

△: Slight whitening is observed.

25 ×: Remarkable whitening and etching at the surface
are observed.

(*6) Hot and cold repeating test: A slate plate was coated
with "ALES GUM TILE Sealer" (manufactured by Kansai Paint Co.,
Ltd., a sealer) in an amount of 150 g/m² by means of a brush,
overcoated under draw-painting with "ALES Rubber Tile Rough"

(manufactured by Kansai Paint Co., Ltd., a thickness-
imparting main agent for outside of a building) by means of a
2 mm blade, and allowed to stand for 24 hours. Then, after
the coated plate was coated with each cold setting coating
5 composition in an amount of 120 g/m² by means of a brush and
allowed to stand for 4 hours, the plate was overcoated with
the same cold setting coating composition in an amount of 120
g/m² by means of a brush to form a test coated plate. The
test coated plate was subjected to a test according to a hot
10 and cold repeating test of JIS A-6909, one cycle of which
comprises <immersion in water for 18 hours - cooling in a
constant-temperature bath of -20°C for 3 hours - heating in a
constant-temperature bath of 50°C for 5 hours>. After the
test of 15 cycles, the state of the coated surface was
15 observed by eye.

◎: No change

○: Slight swelling is observed.

△: Crack and swelling are observed at a part of the
plate.

20 ×: Remarkable crack and swelling are observed all
over the plate.

Table 1

				Example				Comparative Example
				1	2	3	4	1
Coating mixture	Pigment dispersion	Resin solution	Kind	A-1	A-2	A-3	A-4	a-1
			Amount	60	60	60	60	54
		Titanium white		108	108	108	108	108
		Mineral spirit		75	75	75	75	81
	Resin solution		Kind	A-1	A-2	A-3	A-4	a-1
			Amount	240	240	240	240	216
	Cobalt naphthenate			0.4	0.4	0.4	0.4	0.4
	Lead naphthenate			1.4	1.4	1.4	1.4	1.4
Performance tests	Initial dryness			○	○	○	○	○
	Gloss of the coated film			◎	◎	○	○	△
	Weathering resistance			○	○	○	◎	△
	Water resistance			○	○	○	○	○
	Acid resistance			○	○	○	○	○
	Hot and cold repeating test			○	○	◎	○	△

Preparation of Coating Composition

Example 5

- 5 Using the urethane-modified vinyl resin solution (A-5) and the polymer dispersion liquid (B-1) obtained in the above Production Examples, a coating composition was obtained by mixing the components at the mixing composition shown in Table 2 (shown by solid matters), adding 0.3% by weight of
- 10 cobalt naphthenate and 1.0% by weight of lead naphthenate as curing catalysts based on the total resin solid matter, stirring the whole to form a homogeneous mixture, mixing with 20 parts of mineral spirit, 40 parts of "JR603" (TAYCA Corporation, titanium white), 2 parts of "DISPARLON 6900-10X"
- 15 (manufactured by Kusumoto Chemical Co., Ltd., a sagging inhibitor) and 0.8 part of "BYK-066" (manufactured by BYK-Chemie Co., a defoaming agent), dispersing the whole in a sandmill, and controlling the viscosity to 75 to 90 KU with

mineral spirit.

Examples 6 to 12 and Comparative Examples 2 and 3

Each coating composition was obtained in a similar manner to Example 5 with the exception that the composition was changed to each mixing composition shown in Table 2 (shown by solid matters).

Table 2

		Example								Comparative Example	
		5	6	7	8	9	10	11	12	2	3
Urethane-modified vinyl resin	Kind	A-5	A-5	A-5	A-6	A-5	A-5	A-7	A-8	A-9	
	Amount	50	50	50	50	50	50	50	50	50	
Polymer dispersion	Kind	B-1	B-2	B-3	B-1	B-1	B-1	B-1	B-1	B-1	B-1
	Amount	50	50	50	50	50	30	50	50	50	100
Cobalt naphthenate		0.3	0.3	0.3	0.3		0.3	0.3	0.3	0.3	0.3
Lead naphthenate		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Manganese naphthenate						0.3					
Mineral spirit		20	20	20	20	20	20	20	20	20	20
JR603		40	40	40	40	40	40	40	40	40	40
Disparlon 6900-10X		2	2	2	2	2	2	2	2	2	2
BYK-066		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

Further in Comparative Example 2, the following acrylic resin solution (Note 4) was used instead of the urethane-modified vinyl resin solution.

(Note 4) Into a flask was charged 80 parts of mineral spirit, followed by the elevation of temperature to 110°C under stirring with introducing nitrogen gas. Then, a mixture of:

styrene	25 parts
n-butyl methacrylate	12 parts
i-butyl methacrylate	43 parts
2-ethylhexyl acrylate	20 parts
2,2'-azobisisobutyronitrile	1.5 parts

was added dropwise thereto over a period of 4 hours with

maintaining the temperature at 110°C. Then, after the temperature was elevated to 120°C, the mixture was aged for 2 hours to obtain an almost colorless clear viscous acrylic resin solution (A-9), 55% of which was nonvolatile matter.

5 Performance Tests

Upon each cold setting coating composition obtained in the above examples 5 to 12 and Comparative Examples 2 and 3, storage stability was evaluated by observing the state of the coated film after an one month storage at 40°C (○: no change). Furthermore, various tests were carried out according to the following test methods. The test results were shown in following Table 3.

Table 3

	<u>Example</u>								<u>Comparative Example</u>	
	5	6	7	8	9	10	11	12	2	3
<u>Storage stability</u>	○	○	○	○	○	○	○	○	○	○
<u>Initial dryness</u>	○	◎	◎	◎	○	○	○	○	○	◎
<u>Workability at twice coating</u>	○	○	○	○	○	○	○	○	×	△
<u>Gloss of the coated film</u>	○	○	○	○	○	○	○	○	○	×
<u>Water resistance</u>	○	○	○	○	○	○	○	○	○	○
<u>Acid resistance</u>	○	○	○	○	○	○	○	○	○	○
<u>Alkali resistance</u>	○	○	○	○	○	○	○	○	○	○
<u>Hot and cold repeating test</u>	○	○	○	○	○	○	○	○	△	×
<u>Elongation rate (%)</u>	52	41	33	50	53	65	45	70	50	20

Test Methods

15 (*7) Initial dryness: After a glass plate was coated with each composition by means of a 300 μm applicator, the finger-contact dryness of the coated film after standing at 20°C under 75% RH for 6 hours was determined.

◎: No fingerprint is marked.

20 ○: Slight fingerprint is marked.

△: Fingerprint is marked.

×: The coated film adheres to finger.

(*8) Workability at twice coating: A glass plate was coated with each composition by means of a 300 μm applicator, and then the whole was allowed to stand at 20°C under 75% RH for 6 hours. Thereafter, each composition was again applied thereon by means of a brush so as to form a film having a dry thickness of 80 to 100 μm and then the state of the coated film was observed.

○: no change

△: Shrinkage of the coated film is observed.

×: The coated film of the first coating is re-dissolved and therefore the brushing at coating becomes heavy.

(*9) Gloss of the coated film: After a slate plate coated with "ALES CELA MILD" (manufactured by Kansai Paint Co., Ltd., a white mat coating) was coated with each cold setting coating composition by means of a 300 μm applicator and the whole was dried for 1 week, a 60° specular reflection rate was determined, and the case of 80% or more was marked ○ and the case of less than 80% was marked ×.

(*10) Water resistance: After a slate plate was coated with each composition by means of a 300 μm applicator and the whole was dried at room temperature, the state of the coated film after immersing the coated plate in a tap water (20°C) for 3 days was observed.

○: No change

△: Slight swelling is observed.

×: Remarkable swelling is observed.

(*11) Acid resistance: On the coated plate obtained as in

(*7) was added dropwise 0.5 cc of 0.1N sulfuric acid aqueous solution, and after standing at 20°C for 24 hours, the state of the coated plate after washing was observed.

O: No change

5 Δ: Slight whitening is observed.

×: Remarkable whitening and etching at the surface are observed.

(*12) Alkali resistance: On the coated plate obtained as in (*7) was added dropwise 0.5 cc of 0.1N sodium hydroxide aqueous solution, and after standing at 20°C for 24 hours, the state of the coated plate after washing was observed.

O: No change

Δ: Slight whitening is observed.

15 ×: Remarkable whitening and etching at the surface are observed.

(*13) Hot and cold repeating test: A slate plate coated with "ALES HOLDER G II" (manufactured by Kansai Paint Co., Ltd., a white slightly elastic primer) was coated with each coating composition whose viscosity was controlled to 70 KU with mineral spirit, in an amount of 200 g/m² by means of a roller and the whole was dried for 14 days to form a test coated plate. The test coated plate was subjected to the test according to a hot and cold repeating test of JIS A-6909, one cycle of which comprises <immersion in water at 20°C for 18 hours - cooling in a constant-temperature bath of -20°C for 3 hours - heating in a constant-temperature bath of 50°C for 5 hours>. After the test of 10 cycles, the state of the coated surface was observed by eye.

O: No change

△: Crack is observed at a part of the plate.

×: Remarkable crack is observed all over the plate.

(*14) Elongation rate of the coated film: After a release paper was coated with each composition by means of a 300 μm applicator and dried at room temperature for 7 days, a free film having 5 mm width x 20 mm length was collected and an elongation rate (%) was measured after the coated film was drawn at a rate of 10 mm/minute.

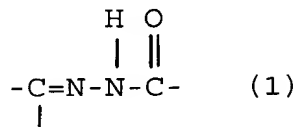
The coating composition of the present invention improves weathering resistance and water resistance of the resulting coated film and further improves crack-following ability of the undercoat by using an oxidatively curable urethane-modified vinyl resin as a film-forming component. Accordingly, the coating composition of the present invention serves extremely excellent effects when used for outside of a building, particularly for inorganic building materials.

Although only some exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciated that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention.

The disclosure of Japanese Patent Application Nos. 2000-069881 and 2000-075653 filed March 14, 2000 and March 17, 2000 respectively, including specification the specifications, drawings and claims, [are] is herein incorporated by reference in [its] their entirety.

ABSTRACT OF DISCLOSURE

[A curable composition, which can be easily decomposed and removed by means of a mixed solution of acid, water, and optionally an organic solvent, is provided. The curable composition contains a resin (A) having a structure of structural formula represented by formula (1)



and crosslinkable functional group(s) in one molecule.]

A cold setting coating composition of this invention comprises an urethane-modified vinyl resin (A) produced by reacting a reaction product with an isocyanate group-possessing compound (c). The reaction product is produced by reacting an epoxy group-containing vinyl copolymer (a) with a fatty acid component (b) containing an unsaturated fatty acid. The vinyl copolymer (a) is a copolymer of a first polymerizable unsaturated monomer containing an epoxy group and a second polymerizable unsaturated monomer. The coating composition improved weathering resistance and water resistance of the resulting coated film.

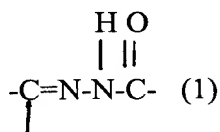
APPENDIX III

MARKED-UP VERSION OF CLAIMS

APPENDIX III

Please cancel claims 1-9 and add claims 10-20 as follows (all of the pending claims are reproduced below in their entirety for the Examiner's convenience):

[1. A curable composition comprising a resin (A) having a structure represented by formula (1):



and

a crosslinkable functional group in a molecule of the resin (A).

2. The curable composition according to claim 1, the structure is formed by reaction of a carbonyl group with one group of a hydrazide group and a semicarbazide group.

3. The curable composition according to claim 1, the crosslinkable functional group in the resin (A) is one type or two or more types selected from a polymerizable double bond, hydroxyl group, carboxyl group, isocyanate group, amino group, thiol group, epoxy group, triazine group, dimide group, silanol group, alkoxysilyl group, methylol group, alkylmethylol group, acetoalkoxy group, carbonyl group, hydrazide group, blocked isocyanate group, blocked carboxyl group and blocked hydroxyl group.

4. The curable composition according to claim 1, the resin (A) has at least one said structure represented by the formula (1) between the crosslinkable functional groups.

5. The curable composition according to claims 1, the resin (A) contains the structure of the structural formula represented by the formula (1) in a backbone of the resin (A) and the crosslinkable functional group in a side chain of the resin (A).

6. The curable composition according to claim 1, the crosslinkable functional group is combined with a backbone of the resin (A) through the structure of the structural formula represented by the formula (1).

7. The curable composition according to claim 1, the resin (A) has same number of the structure of the structural formula represented by the formula (1) and the crosslinkable functional group.

8. A curable composition comprising the resin (A) according to claim 1 and a crosslinking agent (B) reactive to the crosslinkable functional group.

9. An ink, paint, or adhesive containing the curable composition according to claims 1.]

1. A cold setting coating composition comprising an urethane-modified vinyl resin (A) produced by reacting a reaction product with an isocyanate group-possessing compound (c), the reaction product is produced by reacting an epoxy group-containing vinyl copolymer (a) with a fatty acid component (b) containing an unsaturated fatty acid,

said vinyl copolymer (a) is a copolymer of a first polymerizable unsaturated monomer containing an epoxy group and a second polymerizable unsaturated monomer.

2. The cold setting coating composition according to claim 1, wherein the vinyl copolymer (a) is produced by copolymerizing 3 to 70% by weight of the first polymerizable unsaturated monomer containing an epoxy group with 30 to 97% by weight of the second polymerizable unsaturated monomer.

3. The cold setting coating composition according to claim 1, the vinyl copolymer (a) has a number average molecular weight of 1,000 to 100,000 and a glass transition temperature of 0 to 100°C.

4. The cold setting coating composition according to claim 1, the fatty acid component (b) has an iodine value of 50 to 200.

5. The cold setting coating composition according claim 1, wherein a ratio of the fatty acid component (b) is from 1 to 60 parts by weight based on 100 parts by weight of the vinyl copolymer (a).

6. The cold setting coating composition according claim 1, wherein an equivalent ratio of isocyanate group contained in the isocyanate group-possessing compound (c) to hydroxyl group contained in the reaction product (NCO/OH) is from 0.05 to 2.0.

7. The cold setting coating composition according claim 1 further comprises a polymer dispersion (B) obtained by polymerizing two or more of vinyl monomers in the presence of a dispersion stabilizer (d) in an organic liquid in which vinyl monomers are soluble and a polymer formed from the monomers is insoluble, wherein the dispersion stabilizer (d) is soluble in the organic liquid.

8. The cold setting coating composition according to claim 7 comprises 10 to 90% by weight of the urethane-modified vinyl resin (A) and 90 to 10% by weight of the polymer dispersion (B) based on total solid matter weight of the resin (A) and the dispersion (B).

9. The cold setting coating composition according claim 7, the dispersion stabilizer (d) is a resin having an oxidatively polymerizable double bond.

10. (Newly added) The cold setting coating composition according claim 9, the resin having an oxidatively polymerizable double bond is obtained by copolymerizing 5 to 70% by weight of a vinyl monomer having an oxidatively polymerizable double bond and 30 to 95% by weight of another vinyl monomer.

11. (Newly added) The cold setting coating composition according claim 7, at least one of two or more of vinyl monomers is a multi-vinyl compound.